



## PERSPECTIVE

# On the presence of surface bound hydroxyl species on polycrystalline Pt electrodes in the “hydrogen potential region” (0–0.4 V-RHE)



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## 1. Introduction

The hydrogen oxidation reaction (HOR) and evolution reaction (HER) on platinum electrodes have been studied since the 1920s [1], and are essential components of commercial hydrogen fuel cell and water electrolysis devices. Elementary hydrogen adsorption and desorption processes dictate HOR and HER performance. Hydrogen adsorption/desorption has been studied with cyclic voltammetry since the 1960s, with Will reporting voltammograms of polycrystalline and single-crystal Pt in aqueous electrolytes in 1965 [2]. Despite the long history of studies of hydrogen electrochemistry on Pt electrodes, the assignment of voltammetric features to elementary processes and specific Pt facets continues to be debated. In this Perspective article, we summarize the evidence to argue that the low potential “hydrogen region” of the Pt cyclic voltammograms in aqueous electrolytes includes the adsorption/desorption of hydroxyl species on non-1 1 1 facets of Pt.

Fig. 1a shows a typical cyclic voltammogram (CV) for a polycrystalline Pt electrode in aqueous electrolyte. The region between 0 and 0.4 V-RHE (relative to a reversible hydrogen electrode) is referred to as the “hydrogen region” (see e.g. the seminal textbook by Bard and Faulkner [3]) where reversible redox features are typically attributed to H desorption (positive scan) and adsorption (negative scan):



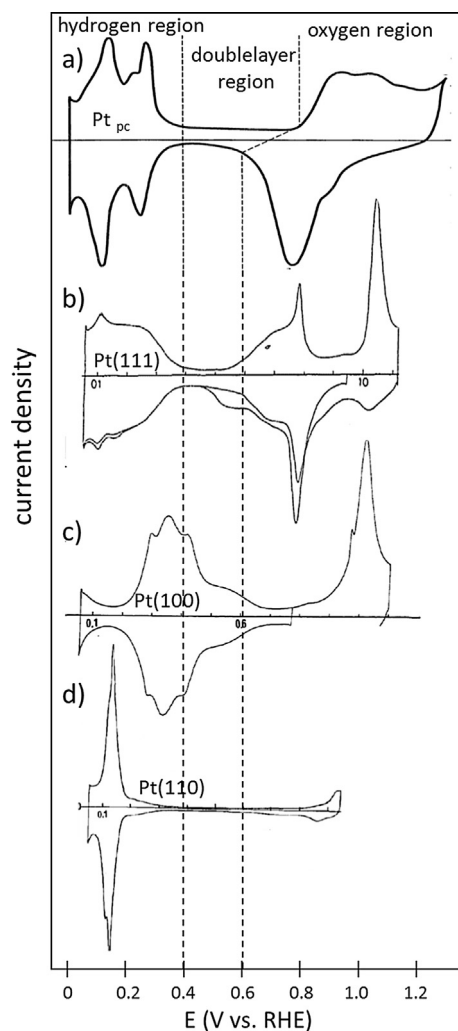
No Faradaic processes occur between 0.4 and 0.6 V-RHE. Redox features at higher potentials are attributed to water oxidation, and referred to as the “oxygen region” with features attributed to surface OH<sup>\*</sup> formation, O<sup>\*</sup> formation, surface PtO<sub>x</sub> formation, and bulk PtO<sub>x</sub> formation [7].

Focusing on the 0–0.4 V-RHE region, two peaks are observed on top of a broader feature, for the polycrystalline Pt electrode. Single-crystal work on (1 1 1), (1 1 0), and (1 0 0) facets has helped to attribute the observed CV features to different Pt facets, with significant contributions dating back to Will's work in the 1960s [2], Clavilier's detailed work in the 1980s [4,6,8,9], and more recent contributions from Feliu's work [10–12]. This single crystal work has attributed the first sharp CV feature (~0.15 V-RHE in acidic electrolyte) to 1 1 0 facets, the second sharp feature (~0.3 V-RHE) to 1 0 0 facets, and the broad feature (spanning 0–0.4 V-RHE) to 1 1 1 facets. Fig. 1b–d show examples of the 1 1 1, 1 0 0, and 1 1 0 CVs from Clavilier and co-workers [4–6]. Higher index facets of Pt show features that are decomposed into contributions from these low index terraces and steps (Fig. 2a–c), with steps having local Pt atom arrangements equivalent to 1 1 0 and 1 0 0 facets showing CV peaks in the same potential ranges [13]. Step-associated peaks are typically sharper than those associated with the extended 1 0 0 and 1 1 0 facets, though we will gloss over this distinction as well as subtle features seen in the single-crystal CVs. Ultra-high vacuum studies of stepped Pt facets similarly show temperature-programmed desorption behavior that can be decomposed into contributions from low index facets [14], confirming that the adsorbate-surface interactions giving rise to these features are attributable to the local arrangement of Pt atoms.

The low-potential (0–0.4 V-RHE) CV peaks associated with the 1 1 0 and 1 0 0 steps or facets shift, on a RHE scale, when changing from HClO<sub>4</sub> (acidic) to NaOH (basic) electrolytes. The broad 1 1 1 peak is relatively unaffected by changes in aqueous electrolyte composition. This is illustrated in Fig. 2a–c, where a positive voltage shift of 0.1–0.2 V occurs with change from low to high pH for the step-associated peaks on Pt(5 5 3) (with 1 1 0 steps) and on Pt(5 3 3) (with 1 0 0 steps) [13]. The cause of these shifts has not been definitively identified. Our groups have demonstrated that the 1 0 0 and 1 1 0-associated shifts, in fact, depend on the solution phase cation concentration, not the pH [16,17]. The observed shift of these peaks with pH has been correlated with changes in the HOR rate [18–20].

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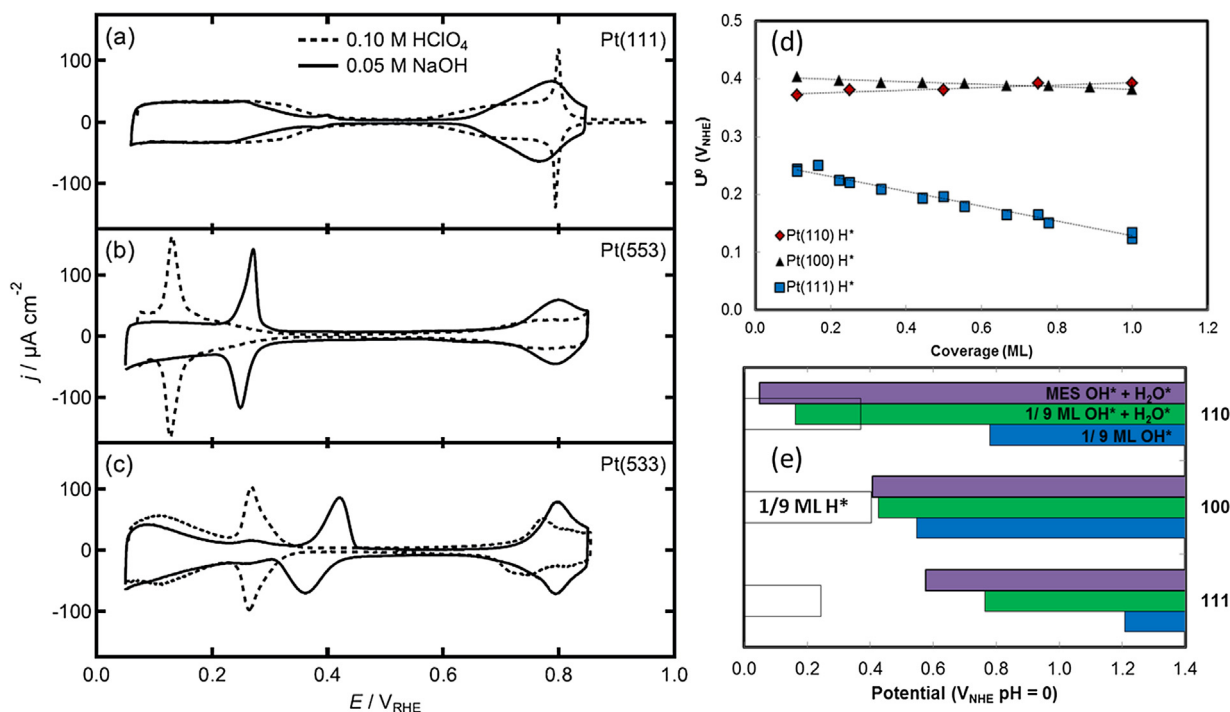


**Fig. 1.** Cyclic voltammograms of (a) a polycrystalline Pt electrode (adapted from Bard and Faulkner [3]), (b) Pt(1 1 1) (adapted from Clavilier et al. [4]), (c) Pt(1 0 0) (adapted from Rodes et al. [5]), and (d) Pt(1 1 0) (adapted from Armand and Clavilier [6]) in acidic solutions.

Despite the textbook reference of 0–0.4 V-RHE as the “hydrogen region,” and the detailed single crystal studies on Pt electrodes, attribution of the voltammetric features to elementary surface phenomena remain debated. The Yan group has used the “pH-induced shifts” in the 1 1 0 and 1 0 0-associated peaks as a measurement of the “apparent hydrogen binding energy,” attributing these peaks to adsorption/desorption of H atoms from the surface, potentially combined with changes in the amount or structure of adsorbed water molecules [19,21,22]. Density functional theory (DFT) models of the electrochemical interface have been used to attribute the “pH-induced shift” to changes in water adsorption or structure at the interface, furthering the allocation of voltammetric features to hydrogen adsorption/desorption [21,23]. We provided a contrasting view, showing that the “pH-induced shifts” do not arise directly from changes in pH, but instead from changes in the near-surface cation concentration that is a combined consequence of the solution phase cation concentration and pH. We used DFT results to attribute these shifts to the effect of cations on hydroxide adsorption that follows H desorption on (1 0 0) and (1 1 0) features [15–17]. The essential difference in these explanations is whether the low potential peaks on 1 0 0 and 1 1 0 features are attributed to H adsorption/desorption, or to a collective process in which H adsorption/desorption occurs with concurrent desorption/adsorption of surface bound hydroxyl species. Either process could also include changes in the interactions of interfacial electrolyte with the Pt surface.

Beyond the significance of changing the textbook attribution of these features to solely H-processes, the inclusion of hydroxyl adsorbates in these low potential features has implications for explaining the pH-dependent HOR chemistry, interpreting alcohol or CO oxidation behavior, or using voltammetry to measure Pt electrode surface area. This significance has motivated us to summarize here the evidence that surface hydroxyl species are involved in these low potential features on the non-1 1 1 Pt facets. A number of experimental observations, as well as DFT data, support the conclusion that hydroxide is adsorbed in the “hydrogen region” on non-1 1 1 surfaces.

The relative positions of the CV peaks among the 1 0 0, 1 1 0, and 1 1 1 facets do not align with where they would be expected based on relative H surface binding energies. Clavilier noted in the 1980s that “a direct comparison between the gas phase binding energy and the adsorption potential does not seem possible” as “the potential sequence for the respective hydrogen states gives the inverse order” in comparison to gas phase hydrogen adsorption energies [8]. For oxidation of adsorbed H atoms to form a solution phase proton, a more positive potential is indicative of stronger binding to the surface. As observed in Fig. 1, this would suggest that the binding strength of H to 1 1 0 is weaker than 1 0 0, and the broad peak on 1 1 1 would suggest binding energies spanning those of 1 1 0 and 1 0 0. Temperature programmed desorption (TPD) data from ultra-high vacuum (UHV) studies on Pt surfaces indicates higher desorption temperatures (consistent



**Fig. 2.** Voltammetry and DFT studies of  $\text{H}^+$  and  $\text{OH}^+$  species on Pt electrodes. Cyclic voltammetry profiles of (a) Pt(1 1 1), (b) Pt(5 5 3) which includes 1 1 0-like steps, and (c) Pt(5 3 3) which includes 1 0 0-like steps. CVs taken in 0.1 M  $\text{HClO}_4$  and 0.05 M  $\text{NaOH}$  solutions at  $50 \text{ mV s}^{-1}$  [13]. (d) DFT-calculated equilibrium adsorption potentials ( $U^0$ , V-NHE) for the adsorption of hydrogen from a pH = 0 solution as a function of coverage (ML) onto Pt(1 1 1) (blue square), Pt(1 0 0) (black triangle), and Pt(1 1 0) (red diamond) [15]. (e) Favorable adsorption potentials ranges ( $V_{\text{NHE}}$ ) based on DFT calculations for hydrogen (1/9 ML, white bar) and hydroxide adsorption (1/9 ML, blue bars; 1/9 ML with solvating  $\text{H}_2\text{O}$ , green bars; minimum energy structures (MES), purple bars) on Pt(1 1 1), Pt(1 0 0), and Pt(1 1 0) surfaces [15]. MES for Pt(1 1 1) and Pt(1 0 0) are 1/3 ML  $\text{OH}^+$  and 1/3 ML  $\text{H}_2\text{O}^+$  and for Pt(1 1 0) is 1/2 ML  $\text{OH}^+$  and 1/2 ML  $\text{H}_2\text{O}^+$ .

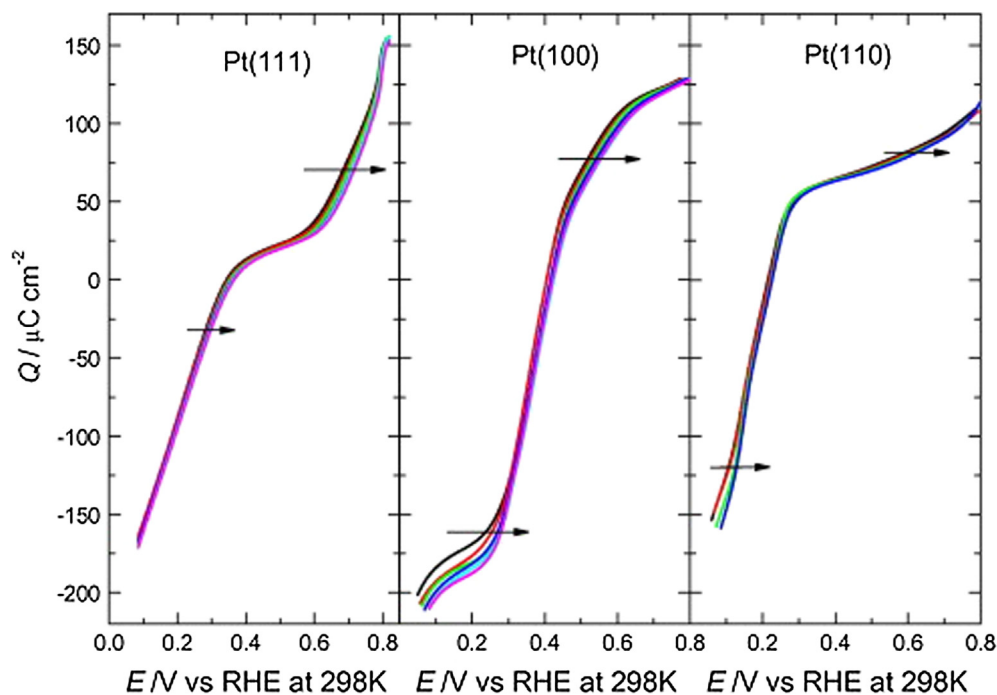
with stronger binding) and a narrower desorption peak (consistent with a weaker coverage dependence) on Pt(1 0 0) and 1 0 0 steps than on Pt(1 1 1) and 1 1 1 terraces [14,24–26]. DFT calculations show that adsorption is stronger to 1 0 0 and 1 1 0 facets than to 1 1 1 [15,27,28], agreeing with peak ordering from UHV TPD studies. Fig. 2d shows the DFT calculated equilibrium potentials for H adsorption/desorption from 1 1 1, 1 0 0, and 1 1 0 facets as a function of H coverage. If the relative peak positions were dictated by H binding energies alone, DFT and UHV studies suggest a broad peak for Pt(1 1 1) that is at lower potential than Pt(1 0 0) and Pt(1 1 0), and that the 1 0 0 and 1 1 0 peaks should overlap. As the CV peaks are highly reversible, the kinetics of the adsorption/desorption processes cannot account for the discrepancy in order between UHV and the electrochemical environment. Either other adsorbed species are involved in the electrochemical processes, or the electrochemical environment must alter the relative binding energies of H to the different facets. As we will discuss below, treating the peaks on 1 1 0 and 1 0 0 as representative of H adsorption/desorption coupled with hydroxyl desorption/adsorption leads to a peak ordering that matches voltammetry.

The potential ordering of the high potential “O region” peaks across the 1 1 0, 1 0 0, and 1 1 1 facets is similarly counterintuitive, if the onset of these peaks are to be assigned to surface hydroxyl formation. All three electrodes show a “double-layer region” between the low-potential “hydrogen region” and high potential “oxygen region” (Fig. 2a–c). The “oxygen region” begins at the lowest potential on Pt(1 1 1), with higher potentials required to see features on 1 0 0 and 1 1 0 facets. Lower potentials of hydroxyl or oxygen adsorption would indicate greater stability of  $\text{OH}^+$  or  $\text{O}^+$  surface species. The experimental “oxygen region” peak potential order, if taken to indicate relative stability of surface hydroxyl species, again inverts the expected peak order based on stability of surface hydroxyls. TPD studies of mixed O and  $\text{H}_2\text{O}$  adsorbates have been used to rank the relative binding energy of  $\text{OH}^+$  in the order of increasing binding strength as: Pt(1 1 1) or 1 1 1 terraces ( $\sim 200 \text{ K}$  desorption peak [29–31]) < the 1 1 0-like step on Pt(5 5 3) (234 K desorption peak [30]) < the 1 0 0-like step on Pt(5 3 3) (270 K desorption peak [31]). DFT results confirm this ordering, also indicating that  $\text{OH}^+$  binds stronger to the less coordinated 1 0 0 and 1 1 0 facets. The DFT calculated equilibrium adsorption potentials in Fig. 2e show that hydroxyl adsorption (1/9 monolayer, blue potential ranges) to 1 0 0 is most favorable, followed by 1 1 0 with weakest binding to 1 1 1. Inclusion of solvation in the model of surface bound OH makes 1 1 0 adsorption most favorable, followed by 1 0 0 and 1 1 1. Both the TPD and DFT  $\text{OH}^+$  stability orders, therefore, do not predict the lower potential onset in the “oxygen region” for the Pt(1 1 1) electrode compared to 1 1 0 or 1 0 0 features. Perhaps more importantly, the DFT adsorption equilibrium potentials suggest a clear overlap of surface H and surface OH regions on Pt(1 1 0), partial overlap on Pt(1 0 0), and a pronounced double-layer region on Pt(1 1 1).

The order of low potential CV features can be easily explained by considering that a  $\text{H}^+/\text{OH}^+$  exchange process accounts for these features on 1 1 0 and 1 0 0 facets and steps:



Voltammetric features in the traditional “hydrogen region” have been attributed to this exchange reaction on Ru(0 0 0 1) [32], Pt-Ru close-packed surfaces [33], and Ir(1 1 1) [34,35]. The favorability of  $\text{OH}^+$  adsorption at relatively low potentials on the Pt(1 1 0) surface pushes the



**Fig. 3.** Charge density plots derived from CO displacement studies for Pt(1 1 1), Pt(1 0 0) and Pt(1 1 0) in 0.1 M HClO<sub>4</sub> at temperatures between 273 and 323 K for Pt(1 1 1) and Pt(1 0 0), and between 283 and 313 K for Pt(1 1 0). Arrows indicate the effect of increasing temperature. Figure taken from [12].

equilibrium potential for reaction (2) to a lower potential than that for H<sup>+</sup> adsorption/desorption alone (reaction (1)). The exchange reaction on 1 1 0 is also predicted to occur at lower potential than H<sup>+</sup> adsorption/desorption on 1 1 1 or 1 0 0 facets, explaining why the 1 1 0-associated sharp feature occurs at the lowest potential. The replacement process is also favorable at similar potentials to H<sup>+</sup> adsorption/desorption on 1 0 0 features. A detailed thermodynamic analysis of the low potential peaks also demonstrated a fit to overlapping H<sup>+</sup> and OH<sup>-</sup> regions on 1 0 0 and 1 1 0 facets [12]. Experimental charge densities for low potential features on stepped surfaces are consistent with an exchange of 1 e<sup>-</sup> per surface Pt atom on 1 1 1 terraces, but ~1.3 on stepped surfaces due to the additional charge associated with converting 1 ML of H<sup>+</sup> to 1/3 ML of OH<sup>-</sup> on the steps [36]. The sharpness of the (1 0 0), (1 1 0), and step-associated features is also consistent with Monte Carlo models of the H/anion exchange reaction, in which the adsorbed H<sup>+</sup> and adsorbed anion interact repulsively [37]. The evidence presented here effectively shows that the presence of water to solvate OH<sup>-</sup> allows for simultaneous H<sup>+</sup> and OH<sup>-</sup> adsorption on all non-1 1 1 facets. The favorability of dissociative water adsorption to form co-adsorbed H<sup>+</sup> and OH<sup>-</sup> has been shown on Pt(5 3 3) in the absence of solvation [38], and solvation only further facilitates overlapping adsorption potentials. Our previous experimental and DFT work has shown that this exchange reaction, and the effects of cation co-adsorption on surface OH<sup>-</sup> stability, can fully explain shifts in 1 0 0 and 1 1 0-like step features from pH 3 to pH 13 as being due to cation-hydroxide interactions [16,17]. Further, these peaks do not shift in the absence of alkali metal cations between pH 0 to 3.

Based on the above arguments, assigning the low potential peaks to reaction (1) alone would require the adsorption favorabilities of H<sup>+</sup> and OH<sup>-</sup> across facets in the electrochemical environment be altered significantly relative to the Pt-vacuum interfaces. This would be in contrast with DFT results that have suggested that solvent and electric field effects on H<sup>+</sup> adsorption are small [28,39]. Assignment of the “hydrogen region” features to H<sup>+</sup> adsorption/desorption alone is also inconsistent with the total charge allocated to these features, and the exchange reaction 3 provides a convenient explanation that then leads to peak positions and total currents that match experiment [13,15,40]. Though TPD and DFT analyses have incorporated some features of the electrochemical interface in examining surface species stability, their imperfections leave it plausible that differences in H<sup>+</sup> OH<sup>-</sup>, or H<sub>2</sub>O<sup>+</sup> interactions within the electrochemical double-layer, and associated double-layer charging, cannot entirely be ruled out as explaining the discrepancies between UHV and electrochemical behavior.

Two pieces of more direct evidence, that suggest OH<sup>-</sup> adsorption in the “H region” on non-1 1 1 facets, are infrared adsorption spectroscopy (IRAS) and carbon monoxide displacement studies. Tanaka et al. used the PtOH bending mode ( $\delta_{\text{PtOH}}$ ) associated with adsorbed OH<sup>-</sup> species to measure the potential dependent adsorption of OH<sup>-</sup> to 1 0 0, 1 1 0, and 1 1 1 Pt electrodes. They observed no OH<sup>-</sup> adsorption in the “hydrogen region” of potential on Pt(1 1 1), but observed OH<sup>-</sup> formation on the surface of Pt(1 1 0) and (1 0 0) electrodes at potentials as low as 0.3 V-RHE [41]. The correlation between the OH<sup>-</sup> IRAS signal and the voltammetric features across facets is imperfect, and suggests difficulty in completely isolating the OH<sup>-</sup> spectroscopic feature. CO displacement studies provide an additional piece of evidence in favor of OH<sup>-</sup> adsorption at low potentials. In these studies, the potential is held constant while CO is introduced, which adsorbs strongly and displaces any adsorbed species from the surface. If the surface is covered in H<sup>+</sup>, CO displacement causes an oxidative current, whereas if the surface is covered in OH<sup>-</sup>, CO motivates OH<sup>-</sup> desorption and a reductive current is observed. Fig. 3 [12] illustrates the total electrode charge as a function of potential determined with CO displacement studies. Pt(1 1 0) shows a transition from an oxidative (negative charge in Fig. 3) process to a reductive process at ~0.2 V-RHE, with Pt(1 0 0) and (1 1 1) showing higher values consistent with their “hydrogen region” voltammetric features. Pt(1 1 1) shows an inflection point suggestive of a double-layer region at potentials just above 0.4 V-RHE, whereas Pt(1 0 0) shows a relatively continuous increase in negative charge suggesting further OH<sup>-</sup> formation. The onset of CO strip-

ping, where CO adsorbed on an electrode surface is oxidatively removed, has been additionally suggested to be an indicator of hydroxide adsorption [18], as the rate limiting step is thought to involve adsorbed hydroxide. However, the thermodynamics and kinetics of CO stripping also depend on the binding strength of CO and the kinetics of the rate limiting step, so while adsorbed hydroxide is necessary for oxidation to proceed, the potential where CO stripping occurs does not uniquely correlate to the onset of hydroxide adsorption.

Recognizing the presence of adsorbed OH<sup>-</sup> in the low-potential “hydrogen region” of polycrystalline Pt electrodes has significant implications for studies of Pt electrochemistry. A few specific implications:

- (1) *Measuring “hydrogen binding energy.”* The first obvious implication is that the position of the 1 0 0 and 1 1 0 peaks cannot be used as an indication of hydrogen binding energy, and should be thought of as a mixed measurement of H<sup>+</sup> and OH<sup>-</sup> stability at the Pt surface. We have previously attributed shifts in these peak positions with solution cation concentration to changes in OH<sup>-</sup> surface stability, not H<sup>+</sup> stability [15–17]. Differences in such peak positions among even late transition metals (for example, Pt, Ir, and Ru) may be more indicative of relative OH<sup>-</sup> binding than they are of relative H<sup>+</sup> binding. We also previously demonstrated that these peak shifts occur due to changes in cation concentration near to the surface, not due to changes in pH [16]. This motivates further consideration of how cations affect surface electrocatalytic processes occurring in the “hydrogen region” or at lower potentials, especially in pH > 3 electrolytes.
- (2) *Measuring electrochemical surface area.* The integrated current in the “hydrogen region” is often used to measure Pt surface area, and recognizing the involvement of reaction 3 in this region requires re-examining how much current should be expected per surface Pt atom. We have previously re-examined surface area measurements in this context [36].
- (3) *Adsorbate induced Pt-restructuring.* The presence of adsorbates can alter the relative stability of different surface facets. The stabilization of the 1 1 0 surface by strongly adsorbed OH<sup>-</sup> at low potentials helps to explain why Pt electrodes restructure upon potential cycling to expose more 1 1 0 features [42] and to restructuring of Pt(1 1 1) to expose island/stepped features [43].
- (4) *HOR kinetics.* The presence of surface bound OH<sup>-</sup> may also impact our interpretation of HOR kinetics, as Markovic and co-workers have suggested the promotion of hydroxyl adsorption leads to improved HOR rates in alkaline conditions [35]. This suggests the possibility that destabilization of surface bound OH<sup>-</sup> accounts for the lower rates of HOR on Pt electrodes in alkaline conditions. Such pH dependence is observed also on Pt(1 1 1) electrodes [44] for which, however, we would expect extremely low amounts of OH<sup>-</sup> on the surface in the HOR region. The mechanistic explanation for the pH dependence of HOR rates on Pt electrodes remains an open question, though the presence of surface bound OH<sup>-</sup> species at HOR potentials should be considered for a possible role in contributing to this phenomena.
- (5) *CO stripping and methanol oxidation.* Adsorbed OH<sup>-</sup> plays an important mechanistic role in CO and methanol oxidation; knowing when OH<sup>-</sup> adsorbs on platinum electrodes could advance our mechanistic understanding of these reactions. Recent evidence shows that alkali metal cations effect the rate of both CO [45] and methanol oxidation [46]. As our work has suggested a strong effect of cations on surface OH<sup>-</sup> stability, the impact of cations on CO and CH<sub>3</sub>OH oxidation may occur through their effect on OH<sup>-</sup>.

We conclude that the formation of OH<sup>-</sup> on the surface of non-Pt(1 1 1) facets, and therefore polycrystalline Pt, occurs within the traditional “hydrogen region” (0–0.4 V-RHE) potential range, and that recognizing this has significant implications when interpreting the mechanistic source of electrocatalytic behavior of Pt electrodes.

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